

The University of Chicago

**COÖRDINATION COMPOUNDS OF PLATINOUS
HALIDES WITH UNSATURATED (ETHYLENE)
SUBSTANCES**

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By
THEODORE ASKOUNES ASHFORD

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[Reprinted from the Journal of the American Chemical Society, 58, 1733 (1936).]

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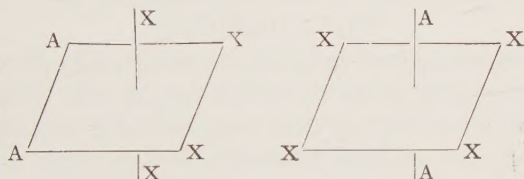
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Coördination Compounds of Platinous Halides with Unsaturated (Ethylene) Substances

Introduction

Platinum is an unusually versatile element. It has primary valences of two and four, and it forms two series of coördination compounds with both organic and inorganic substances. In these the metal exhibits the coördination numbers of four and six, respectively. Stereoisomers have been obtained in both series. Where the coördination number is six, the accepted view is that the valence bonds of the platinum atom are directed toward the corners of an octahedron; giving rise to the following two stereoisomeric configurations for compounds of the type PtX_4A_2 .¹ Some compounds of the type PtX_2A_2 also exist in two stereoisomeric forms: *cis* and *trans*¹ (p. 338).



Furthermore, Reihlen and Hühn² report that they have resolved into optical antipodes platinum compounds of coördination number four. It is still an unsettled question whether the configuration of these compounds is planar, tetrahedral or pyramidal.³

Several classes of coördination compounds of platinum, notably those with ammonia and with the amines, have been studied extensively. However, two important classes, namely, those with unsaturated substances and those with nitriles, have received scant attention because of the lack of satisfactory methods for preparing these complexes.

In the work reported in this paper a particularly simple general method has been developed for the preparation of organo-platinum complexes with unsaturated compounds. This method has been used to prepare a large number of compounds, the properties of which are herein described.

(1) Werner, "Lehrbuch der Stereochemie," Gustave Fischer, Jena, 1904, p. 350.

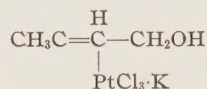
(2) Reihlen and Hühn, *Ann.*, **489**, 42 (1931).

(3) Cf. Dwyer and Mellor, *J. Am. Chem. Soc.*, **56**, 1551 (1934).

Previous Work

The literature contains references to complex salts of the type $\text{K}(\text{Un} \cdot \text{PtX}_3)$, in which Un is an unsaturated molecule containing an ethylene bond. The first compound of this series was obtained by Zeise,⁴ who isolated a substance with the empirical formula $\text{K}(\text{C}_2\text{H}_4 \cdot \text{PtCl}_3) \cdot \text{H}_2\text{O}$, from a reaction mixture of chloroplatinic acid and alcohol. Birnbaum⁵ prepared similar compounds with propylene and amylene, and Chojnacki⁶ obtained $\text{K}(\text{C}_2\text{H}_4 \cdot \text{PtBr}_3)$, with platinic bromide.

Biilmann and his collaborators⁷ have extended the work to unsaturated substances other than hydrocarbons, and they have prepared compounds with unsaturated alcohols, acids and aldehydes. Pfeiffer and Hoyer⁸ have prepared similar substances from allyl alcohol, allyl acetate, crotyl alcohol and crotyl aldehyde. The latter workers consider that in these compounds the platinum atom is coördinately bound directly to the carbon atom by a single bond; they propose the following structure.



This structure indicates that the compounds are derivatives of the metallic chloroplatinates, in which a chloride ion has been replaced by an unsaturated molecule. There is, however, no experimental evidence that the substances are monomolecular.

The series from which the compounds discussed above are derived is obviously $\text{Un} \cdot \text{PtX}_2$. As will be shown later, however, substances of this type are bimolecular and should be written $(\text{Un} \cdot \text{PtX}_2)_2$. Recently, Anderson⁹ obtained $(\text{C}_2\text{H}_4\text{PtCl}_2)_2$ by refluxing ethyl alcohol with sodium chloroplatinate. This reaction is very complex, presumably involving at least four steps. Preliminary at-

(4) Zeise, *Pogg. Ann.*, **21**, 497 (1831).

(5) Birnbaum, *Ann.*, **145**, 67 (1869).

(6) Chojnacki, *Jahresber.*, 510 (1870).

(7) Biilmann, *Ber.*, **33**, 2196 (1900); Biilmann and Anderson, *ibid.*, **36**, 1565 (1903); Biilmann and Hoff, *Chem. Zentr.*, **88**, I, 562 (1917).

(8) Pfeiffer and Hoyer, *Z. anorg. allgem. Chem.*, **211**, 241 (1933).

(9) Anderson, *J. Chem. Soc.*, 971 (1934).

tempts to extend this method to other alcohols have not as yet proved successful.

General Method of Preparation

The most direct method for preparing a compound of the type $(\text{Un} \cdot \text{PtCl}_2)_2$ or $(\text{Un} \cdot \text{PtBr}_2)_2$ would be to combine a platinous halide with an unsaturated compound. However, attempts to apply this method have given unsatisfactory results. Platinous halides are very insoluble and inert substances; consequently platonic halides have been used.

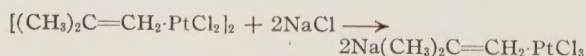
The general method here described departs radically from that of Anderson since anhydrous platonic chloride or bromide in an anhydrous solvent is used instead of the metallic haloplatinates. It differs further in that the unsaturated compounds are used instead of the alcohols. The method is rapid as well as general. The reaction is complete in about an hour.

Although the reaction, as outlined above, and described in more detail in the experimental part, appears simple, it is probably more complex than might at first be supposed. Hydrogen halide is usually evolved during the reaction, and in some instances a small quantity of platinum separates. Halogenation of the unsaturated compound also has been demonstrated.

Physical and Chemical Properties

The coordination compounds $(\text{Un} \cdot \text{PtCl}_2)_2$ are well-defined crystalline substances. When heated in a melting-point tube they do not melt sharply, but darken over a range of several degrees. They vary widely in stability. The greatest difference has been observed between the compounds obtained from *trans*-dichloroethylene and from dipentene. The former decomposes in a few days; the latter appears unchanged even after standing in the air for ten months.

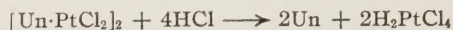
The compounds are in general soluble in acetone, chloroform and alcohol; they are less soluble in benzene, and difficultly soluble or insoluble in glacial acetic acid. Those of low molecular weight are soluble in sodium chloride solution, presumably forming compounds analogous to Zeise's salt



When treated with pyridine the substances decompose, liberating the olefin and forming the pyridine platinous chloride.



Concentrated hydrochloric acid decomposes them.



Bromine also decomposes these substances, forming the platinum halides and the bromine addition product of the unsaturated compound.

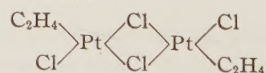
Molecular Weight

The coordination compounds of the series $(\text{Un} \cdot \text{PtCl}_2)_2$ are unstable at higher temperatures; consequently the ebullioscopic method for the determination of their molecular weights is inapplicable. For the same reason the Rast method cannot be used. With the exception of the compound obtained from isobutylene, these substances are also sparingly soluble in benzene. However, the depression of the freezing point of benzene by isobutylene platinous dichloride indicates that the substance is bimolecular, $[(\text{CH}_3)_2\text{C}=\text{CH}_2 \cdot \text{PtCl}_2]_2$, and no doubt the other compounds of the same series are likewise.¹⁰

Structure of the Compounds of the Type $[(\text{Un} \cdot \text{PtCl}_2)]_2$

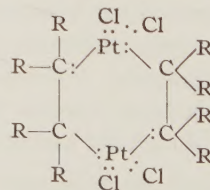
That these compounds are derivatives of platinous chloride seems fairly well established. Their analyses as well as their reactions with pyridine, with concentrated hydrochloric acid, and with bromine point to this conclusion. Furthermore, the compound prepared from dipentene and platonic chloride is the same as the one obtained by treating dipentene with platinous chloride in the presence of dry hydrogen chloride.

Anderson⁹ has proposed for ethylene platinous chloride the formula



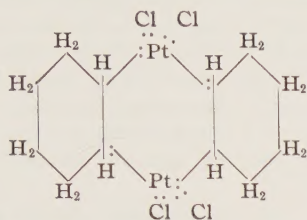
Against this formula, however, may be raised the serious objection that it makes a chlorine atom form two coordination bonds.

Consideration of the electron arrangement in the substance aids in deriving a structure. The general electronic configuration here proposed for all compounds of the type $(\text{Un} \cdot \text{PtCl}_2)_2$

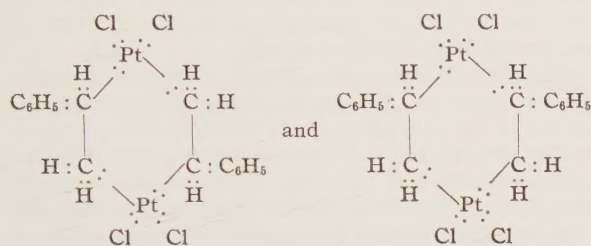


(10) Anderson⁹ has estimated the molecular weight of ethylene platinous chloride by the Barger-Rast method, and his results point to a bimolecular form.

is specifically exemplified in the following formula for cyclohexene platinous chloride



When monosubstituted ethylenes are used, there is a possibility of structural isomerism. For instance, the compound derived from styrene might have either of the two structures shown by the formulas



It is interesting to note that each of these structural isomers contains two asymmetric carbon atoms, and can exist in three stereoisomeric forms. With more complex substituted ethylenes, the number of isomers becomes still greater. Further study of these substances is contemplated.

Applicability of the Method

The method described above has been used to prepare coordination compounds from the following unsaturated substances: cyclohexene, dipentene, pinene, ethylene, isobutylene, styrene, stilbene and *trans*-dichloroethylene. No crystalline coordination compounds could be isolated from the following substances: allyl chloride, allyl bromide, allylbenzene, vinyl bromide, tridecene, isostilbene and *cis*-dichloroethylene. The latter substances react with the platinic chloride to give red solutions but no crystals separate. In all these cases red gums are obtained.

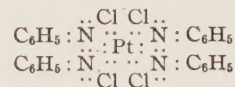
It is interesting that crystalline compounds have been isolated from *trans*-dichloroethylene and from *trans*-diphenylethylene, whereas all attempts to obtain crystalline substances from their *cis*-isomers have failed. It would be desirable to extend the work to other pairs of *cis-trans* stereoisomers, to determine how general this relation is. In this connection it should be noted that from cyclohexene, dipentene and pinene (which are

cis compounds) crystalline substances have been isolated.

The method does not seem to be applicable to unsaturated acids and their esters. All attempts to prepare compounds with maleic anhydride, maleic and fumaric acids and their ethyl esters, and with cinnamic ester have failed. These substances do not appear to react at all with platinic chloride.

Coördination Compound of Platinic Chloride with Azobenzene

It might be expected that azo compounds which contain a double bond between two nitrogen atoms would form coordination compounds similar to those obtained from the olefins. However, the compound obtained from the interaction of platinic chloride and azobenzene has the empirical formula $(\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5)_2\text{PtCl}_4$. This compound is analogous to the coordination compounds of the type $(\text{RCN})_2\text{PtCl}_4$ obtained from platinic chloride and nitriles. It appears that the azo group is equivalent to a nitrile group. For this compound the following formula is proposed



Here one pair of electrons from each azo group forms a coordination bond.

Experimental Part

Preparation of Anhydrous Platinic Chloride.—Anhydrous platinic chloride is prepared by a modification of the method of Rosenheim and Löwenstamm.¹¹ Chloroplatinic acid is prepared by the usual method. The acid melts at about 60° and still contains six molecules of water of crystallization. The melted acid is poured into a porcelain boat and the boat with its contents is placed in a glass tube contained in an electric furnace. A slow current of dry chlorine is passed through the apparatus. The temperature is raised gradually to 275° in the course of two hours; it is kept there for one-half hour and then is allowed to fall gradually. When the apparatus has cooled to about 150°, the boat is removed and the contents are pulverized while hot in an agate mortar. The powdered substance is again placed in the furnace in an atmosphere of chlorine at 275° for one-half hour. It is then allowed to cool and is placed in a glass-stoppered bottle in a desiccator over concentrated sulfuric acid.

Anal. Calcd. for PtCl_4 : Pt, 57.9. Found: Pt, 57.7.

Platinic chloride thus prepared is a very hygroscopic red-brown substance. It is slightly soluble in nitrobenzene, glacial acetic acid and alcohol, very slightly

(11) Rosenheim and Löwenstamm, *Z. anorg. Chem.*, **37**, 403 (1903).

soluble in chloroform and ether, and insoluble in benzene and in toluene.

Preparation of Platinous Chloride.—Platinous chloride is prepared by a modification of the method of Berzelius.¹² Pure chloroplatinic acid is heated over a free flame to about 150°. The resulting solid is placed in a boat, and the boat with its contents is placed inside the furnace. The temperature is raised to 360–380° for about two hours, while a slow current of air is passed through the apparatus. The greenish solid is then pulverized and is again placed in the furnace at 360° for about one hour. After cooling, the solid is boiled with water containing a few drops of hydrochloric acid to remove any unchanged platinum chloride. The platinous chloride, which is insoluble, is washed twice by decantation and again placed in the furnace at 360° for one-half hour.

Anal. Calcd. for PtCl₂: Pt, 73.4. Found: Pt, 73.2.

Platinous chloride is a greenish-gray solid. It is insoluble in benzene, chloroform, glacial acetic acid and alcohol.

General Method of Preparation of Complexes

The most direct method for preparing a compound of the type (Un·PtCl₂)₂ or (Un·PtBr₂) would be to combine a platinous halide with an unsaturated compound. However, attempts to apply this method have given unsatisfactory results. Platinous halides are very insoluble and inert substances; consequently platinum halides have been used.

To prepare the chlorides 0.5 g. of platinum chloride is suspended in 10 cc. of glacial acetic acid and 0.5 cc. (about 2–4 moles) of the unsaturated hydrocarbon is added (in the case of pinene 1 cc. is added). The mixture is warmed in the steam-bath for about ten minutes. During this period the platinum chloride goes into solution and the reaction is completed. Crystals of the chloride separate out from the filtrate with or without cooling and these are collected and washed with additional portions of the solvent. In the case of *cyclohexene* 1 g. of the chloride is triturated with 0.25 g. (1 mole) of the hydrocarbon in 15 cc. of glacial acetic acid and after a few minutes 1 cc. (3 moles) more of the cyclohexene is added, considerable heat being evolved and the reaction going to completion.

In the case of *stilbene* 0.25 g. of the hydrocarbon also is first added and the mixture is heated on the steam-bath, the platinum chloride being completely dissolved in about fifteen minutes to form a red solution. After filtration an additional 0.5 g. (2 moles) of stilbene is added.

Platinic bromide can also be used in place of the chloride and it has the advantage of being more soluble in glacial acetic acid. In the case of *cyclohexene* 0.2 g. of the bromide is dissolved in 5 cc. of glacial acetic acid and 1 cc. of cyclohexene is added. In a few minutes the deep red solution becomes pale orange and long needles separate.

In the case of *styrene* 2 cc. of the hydrocarbon is added to 0.5 g. of the bromide in 10 cc. of glacial acetic acid.

Preparation of Ethylene Platinous Chloride (C₂H₄·PtCl₂)₂.—About 1 g. of platinum chloride is suspended in about 25 cc. of anhydrous benzene. The suspension is kept at 70° for about one hour, while ethylene from a cylinder is bubbled through it. After standing at room

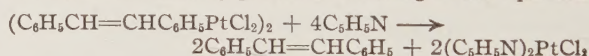
temperature for twenty-four hours, the reaction mixture is again warmed to 70° and treated with ethylene. During these operations most of the platinum chloride goes into solution, and at the same time a considerable quantity of hydrogen chloride is evolved. The hot solution is filtered, and from the filtrate, upon cooling, orange crystals separate. They are crystallized from benzene.

This compound is identical with the one prepared by Anderson⁹ by refluxing absolute alcohol with sodium chloroplatinate.

Preparation of Isobutylene Platinous Chloride [(CH₃)₂C=CH₂·PtCl₂]₂.—About 0.5 g. of platinum chloride is suspended in 10 cc. of glacial acetic acid and the mixture is warmed to 50°. Isobutylene, prepared by heating *t*-butyl alcohol with oxalic acid, is then bubbled through the suspension. In the course of a few minutes the platinum chloride dissolves, giving a red solution. The solution is filtered. As more isobutylene is bubbled through the filtrate orange crystals separate. The crystals are washed with glacial acetic acid.

Molecular Weight.—The solubility of this compound in benzene permits an accurate determination of its molecular weight. The compound is found to be bimolecular: solute, 0.1330, 0.2406, 0.2406 g.; solvent, 8.742, 8.742, 17.484 g.; average depression, 0.119, 0.223, 0.107°. Calcd. for (C₄H₈·PtCl₂)₂: mol. wt., 644.4. Found: mol. wt., 654, 633, 658.

Reaction of Stilbene Platinous Chloride with Pyridine.—About 0.2 g. of stilbene platinous chloride is dissolved in 2 cc. of chloroform and 10 drops of pyridine added. A yellowish precipitate, presumably pyridine platinous chloride, separates. About 25 cc. of petroleum ether is added, and the filtrate is evaporated to dryness. A crystalline substance melting at 125° is obtained. A mixture of this substance with stilbene also melts at 125°. The reaction evidently proceeds according to the equation



Reaction of Stilbene Platinous Chloride with Concentrated Hydrochloric Acid.—About 0.1 g. of stilbene platinous chloride is dissolved in 10 cc. of benzene, and 20 cc. of concentrated hydrochloric acid is added. After shaking for about one hour the mixture is allowed to stand overnight. The benzene layer becomes colorless, while the aqueous layer becomes orange. The benzene layer upon evaporation gives colorless crystals, melting at 125°. A mixture of these crystals with stilbene also melts at 125°. The aqueous layer upon evaporation at 100° gives platinum chloride.

Reaction of Stilbene Platinous Chloride with Bromine.—About 0.3 g. of stilbene platinous chloride is dissolved in 20 cc. of chloroform and an excess of bromine in carbon tetrachloride is added. The solution is then evaporated under reduced pressure. The red mass is extracted with petroleum ether, and the solution after filtering is evaporated to dryness. The solid that is obtained and also a mixture with stilbene dibromide melts at 237°. The residue from the extraction is soluble in water, consisting presumably of platinum chloride and platinum bromide.

Cis-Phenylethylene; Isostilbene.—This substance is prepared by hydrogenation of tolane in methyl alcohol solution in the presence of platinum catalyst, until the theoretical amount of hydrogen is absorbed. Upon

(12) Berzelius, *Schweigger's J.*, 7, 55 (1813).

TABLE I

ORGANO PLATINUM COMPOUNDS: ANALYSES, CHEMICAL, PHYSICAL AND OPTICAL PROPERTIES

Platinous chlorides	Optical data ^a			Ext. angle	Solubilities ^b								NaCl soln.	M.p., °C.	Platinum, %		
	Color	Form	Bire.		CHCl ₃	Ether	Bz	EtOH	Glac. HAc	Acetone	Water				Calcd.	Found	
Cyclohexene	sl. or.	l. silky need-les ^c	...	par. sym. obl.	s.	s.	sl. s.	v. s.	ins.	v. s.	...	ins.	145-146	56.07	56.0	56.0 ⁱ	
Dipentene	f. yel.	biax. pr. ^c	low	34°	v. s.	ins.	v. sl.	ins.	ins.	s.	...	ins.	151-152	48.53	48.4 ^d	48.3 ^{e,j}	
Pinene	f. yel.	prisms ^c	high	6°	v. s.	sl.	s.	sl.	sl.	s.	...	ins.	138-141	48.53	48.6	48.6	
Ethylene	or.	tablets ^c	high	32°	s.	v. s.	s.	v. s.	ins.	v. s.	sl. ^g	sl.	170-180 ^f	66.35	65.7	65.7	
Isobutylene	or.	rhb. pl.	...	18°	v. s.	v. s.	v. s.	v. s.	sl.	v. s.	ins. ^g	v. s.	144-145	60.59	60.6	60.7	
Styrene	or.	hex. pr. ^c	fair	30°	s.	s.	sl.	...	v. sl.	s.	ins.	v. sl.	169-171	52.73	52.6	52.6	
Stilbene	or.	sm. hex. pr. ^c	high	30°	v. s. ^h	s.	v. sl.	v. sl.	ins.	v. s.	...	ins.	191-192	43.75	43.7	43.7 ^k	
<i>trans</i> -Dichloroethylene	or.	cryst. ^c	high	par.	s. ^h	...	s.	...	...	s.	...	...	155-160	53.77	54.6	54.7	
Cyclohexene ·PtBr ₂	or.	l. sl. need. ^c	fair	par.	s.	ins.	v. sl.	v. sl.	ins.	sl.	...	...	150-151	44.66	44.5	44.7	
Styrene- PtBr ₂	rose	hex. pr. ^c	fair	32°	s.	ins.	sl.	ins.	ins.	sl.	...	ins.	153-154	42.52	42.4	42.5	

^a Abbreviations: par., parallel; sym., symmetrical; obl., oblique; ext., extinction; bire., birefringence; or., orange; yel., yellow; f., faint; l., long; sm., small; pl., plates; sl., slender; pr., prisms; hex., hexagonal. ^b Abbreviations: s., soluble; v., very; sl., slightly soluble; ins., insoluble. ^c Anisotropic. ^d Prepared from platinous chloride and dipentene. ^e Prepared from platinic chloride and dipentene. ^f After standing in air for about three weeks it decomposes at 125-130°. ^g Also in petroleum ether. ^h Also in nitrobenzene. ⁱ % Chlorine calcd.: 20.37. Found: 20.34 and 20.44. ^j % Chlorine calcd.: 17.63. Found: 17.7 and 17.7. ^k % Chlorine calcd.: 15.89. Found: 15.8 and 15.8.

evaporation of the solvent an oil is obtained. This oil is dissolved in light petroleum ether (b. p. 30-35°), and placed in acetone-carbon dioxide mixture to precipitate any unchanged tolane. The cold solution is then filtered and the filtrate is evaporated, leaving the pure substance in the form of an oil.

All attempts to prepare crystalline coordination compounds with isostilbene have failed. Nitrobenzene, benzene, chloroform and glacial acetic acid have been used as solvents, and the temperature as well as the time of heating have been varied. In all cases the platinic chloride goes into solution while hydrogen chloride is evolved. Under all conditions red gums have been obtained.

Preparation of *Trans*-Dichloroethylene Platinous Chloride, *trans*-(C₂H₂Cl₂·PtCl₂)₂.—About 0.5 g. of platinic chloride is suspended in 10 cc. of benzene, and 1 cc. of *trans*-dichloroethylene is added. The mixture is warmed to 40-50° for about three hours, during which most of the platinic chloride goes into solution and at the same time a considerable quantity of hydrogen chloride gas is evolved. The reaction mixture is then heated to the boiling point of benzene and filtered. From the filtrate amber crystals separate on cooling.

***Cis*-Dichloroethylene.**—Several attempts to isolate a crystalline compound with *cis*-dichloroethylene have failed. As in the case of *cis*-diphenylethylene gums have been obtained.

Preparation of Di-azobenzene Platinic Chloride (C₆H₅N=NC₆H₅)₂·PtCl₄.—About 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid, a gram of azo-

benzene added to the mixture and the whole warmed on a steam-bath. After about one hour the platinic chloride goes into solution and at the same time a brick-red solid separates. The compound is purified by washing successively with glacial acetic acid, benzene and petroleum ether.

Anal. Calcd. for (C₆H₅N=NC₆H₅)₂·PtCl₄: Pt, 27.84. Found: Pt, 27.5, 27.6.

The compound decomposes at 168-170°.

Solubility.—This compound is soluble in acetone, chloroform and ether; and slightly soluble in glacial acetic acid, alcohol and benzene.

Summary

1. It has been shown that anhydrous platinic halides react with ethylenic substances to give coordination compounds of the type (Un·PtX₂)₂.
2. The behavior of these coordination compounds with various reagents has been described.
3. A ring formula has been proposed for the coordination compounds.

Acknowledgment

The author acknowledges the valuable suggestions of Dr. M. S. Kharasch, under whose direction this research has been conducted.



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